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THE USE OF SORPTION TUBES TO SAMPLE AIR FOR SULFUR DIOXIDE DETERMINATIONS

Abstract

A method for sampling air in a sorption tube to determine SO_2 is proposed. Glass powder (grain sizes 1-2 mm) impregnated with a 2.5% solution of potash containing a 15% non-drying organic additive is recommended for the sorbent. The efficiency with which sorption tubes trap sulfur dioxide when the air aspiration rate is 4 liters/minute is 98-99%. The advantages of sorption tubes over liquid absorption instruments with a porous glass tile include the possibility of passing large volumes of air, compactness, simplicity of manufacture, possibility of sampling air at below freezing temperatures, and low hydrodynamic resistance.

* * *

The first step in the chemical determination of SO_2 in the atmosphere is sampling, involving drawing a known volume of air through an absorption instrument with a porous glass tile containing an absorption solution. The drawbacks in the use of liquid absorption instruments are evaporation of the absorption solution during the sampling process, a particularly significant factor in the summer time, and freezing of the solution when the air temperature is below freezing.

The purpose of the research was to develop a more suitable device for sampling air to be analyzed for SO_2.

Figure 1. Sorption tube.

We considered a number of approaches, and the most likely one appeared to be the use of a solid chemisorbent in the form of glass powder impregnated with an alkaline solution and placed in a small tube with a perforated bottom. The dimensions and shape of the sorption tubes, as well as the quantity and grain diameter of the glass powder with which the tubes were filled, were selected so they would be convenient to work with, and would have a low layer hydrodynamic resistance. Figure 1 is a drawing of the sampling tube used in the experiments.

What the work involved, in essence, was selection of the composition of the solution used for impregnation purposes such that its efficiency in trapping sulfur dioxide would be adequate, and providing an answer to the question of just how complete was the desorption of the absorbed SO_2.

The experiments designed to select the most efficient impregnating solution were conducted with given concentrations of sulfur dioxide, obtained using two types of dynamic metering devices, diffusion and bubbler (Figures 2 and 3).

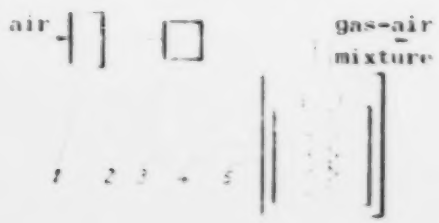

Figure 2. SO_2 diffusion metering device. 1 - microcompressor; 2 - air purifier; 3 - temperature controlled bath; 4 - container with H_2SO_3 solution; 5 - fluorolon-4 diffusion tube.

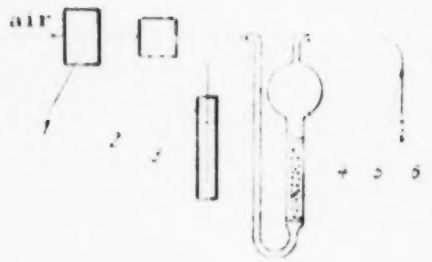

Figure 3. SO_2 bubbler metering device. 1 - microcompressor; 2 - air purifier; 3 - manostat; 4 - saturator; 5 - fluorolon-4 tube; 6 - capillary inleaker.

The efficiency with which the sulfur dioxide was trapped was assessed in terms of how much passed on through the sorption tube. This pass through was measured in two ways:

(1) integrally, using a series connected absorption instrument that trapped all the SO_2 that passed on through the tube during the experiment (Figure 4). The accuracy in the determination of the pass through quantity was $\sim$ 1%;

(2) dynamically, in terms of the magnitude of the SO_2 concentration beyond the tube under test. A special installation was assembled to measure this concentration, and the determination of the SO_2 concentration resulting from its use was very accurate.

The principal component in the installation was a coulometric cell sensitive to sulfur dioxide. The cell was connected to a precision electronic potentiometer. A waterjet pump was used to pull air containing SO_2

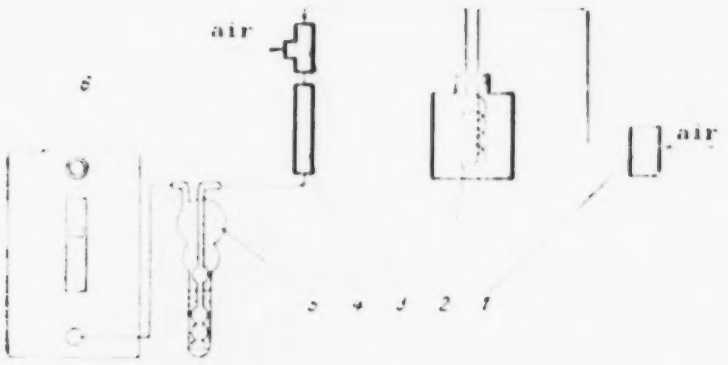

Figure 4. Installation for checking SO_2 trapping efficiency. 1 - microcompressor; 2 - diffusion metering device; 3 - mixer; 4 - sorption tube; 5 - Richter absorption tube; 6 - electrical aspirator.

through the sorption tube being checked, and through the coulometric cell. A needle valve functioning in the critical nozzle mode was used to stabilize the air flow. The accuracy with which the magnitude of the SO_2 that passed through the sorption tube was 0.01% in this case.

A whole series of alkaline impregnating solutions were tested during the experiments. Figures 5-7 show the results of these tests. It was found that aqueous solutions of alkalis, or potash, applied to glass powder, are quite efficient in trapping sulfur dioxide, but only in the moist state. The best results were obtained with an impregnating solution containing an additive of non-drying organic solvents, such as glycerine and ethylene glycol, which provide for 98-99% SO_2 absorption. Solutions

containing ethylene glycol provided more efficient trapping, but only when comparatively small volumes of air (up to several hundred liters) were drawn through the equipment.

Figure 5. Integral passage of SO_2 through the sorption tube (%) as a function of air aspiration rate and glycerine concentration in the solution used to impregnate the sorbent. 1 - 2.5% KOH, 50% glycerine, 47.5% H_2O; 2 - 2.5% KOH, 10% KCl, 50% glycerine, 37% H_2O; 3 - 2.5% KOH, 30% KCl, 8% glycerine, 59.5% H_2O; 4 - 2.5% KOH, 30% KCl, 3% glycerine, 64.5% H_2O; 5 - 2.5% KOH, 30% KCl, 1% glycerine, 66.5% H_2O; 6 - 2.5% KOH, 30% KCl, 67.5% H_2O; 7 - 2.5% KOH, 87.5% H_2O.

A good deal less volatile glycerine proved to be more advantageous when it was necessary to concentrate SO_2 from substantially greater volumes of air. The optimum concentration of ethylene glycol, or glycerine, was established by conducting a special series of experiments,

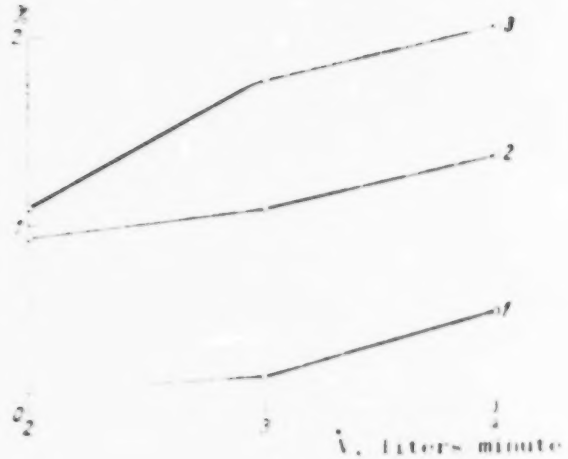

Figure 6. Integral passage of SO_2 through the sorption tube (%) as a function of air aspiration rate and composition of solution for impregnating the sorbent. 1 - 15% ethylene glycol, 3% K_2CO_3, 82% H_2O; 2 - 15% glycerine, 2.5% KOH, 82.5% H_2O; 3 - 15% glycerine, 3% K_2CO_3, 82% H_2O.

the results of which are shown in Figure 8. The data obtained from these experiments revealed that no further significant change in the absorption efficiency could be expected once the glycerine concentration had reached 10-12%, so we stopped using alkaline solutions containing 15% non-drying organic additive.

Once we had obtained satisfactory results by using sorption tubes to trap SO_2 in the air we could proceed to establish the completeness of desorption of the absorbed substance from the tube in the analysis process.

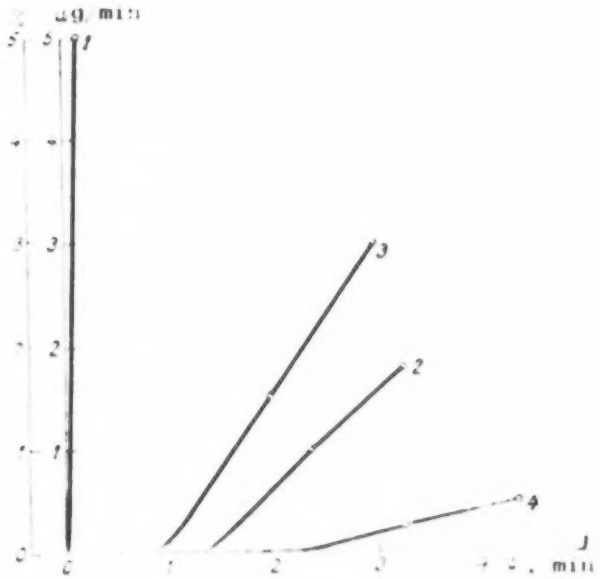

Figure 7. SO_2 concentration beyond the sorption tube as a function of time for various impregnating solutions (air aspiration rate 4 liters/minute). 1 - 15% glycerine, 85% H_2O; 2 - 2.5% KOH, 15% glycerine, 82.5% H_2O; 3 - 3% K_2CO_3, 15% glycerine, 82.0% H_2O; 4 - 3% K_2CO_3, 15% ethylene glycol, 82% H_2O.

Table 1 lists the results of a test made of the tubes for specified SO_2 concentrations. As will be seen from these data, use of the tubes resulted in a determination of a mean of 99% of the specified quantity of SO_2, with a root-mean-square deviation of $\pm$5%.

A special check was made to see if it was feasible to use sorption tubes for sampling purposes when temperatures were below zero. A simple installation, based on the recently suggested, and still little known, method that involves cooling pieces of dry ice with a calcium chloride

Figure 8. Passage of SO_2 through the sorption tube (%) as a function of glycerine content in the solution used to impregnate the sorbent when the air aspiration rate was 2 liters/minute (1), 3 liters/minute (2), and 4 liters/minute (3).

solution [2], was built to cool the tubes to -40°C. This system can automatically maintain the temperature close to the solution freezing point.

The result of the experiments that were laid on was a finding that sorption tubes practically completely trap sulfur dioxide, even at temperatures below zero (Table 2).

An important characteristic of any absorption instrument is the hydrodynamic resistance offered to the flow of air being pulled through. Figure 9 shows the results of a check made of the resistance offered by

Table 1.

COMPLETENESS OF EXTRACTION OF SORBED SO_2 FROM TUBE

Given, μg	Found μg	Found %
32	30	94
	29	91
	30	94
	35	109
	35	109
58	60	103
	55	95
	60	103
	55	95
	58	100
75	74	96
	76	101
	76	101
	74	96
	75	100

the proposed sorption tubes at different air suction rates. Constructed alongside for purposes of comparison is a similar curve for the standard absorption instrument with a No. 1 porous glass tile in use today.

As will be seen from the figure, the resistance of the sorption tube is less by a factor of 5-7, at conventionally used aspiration rates.

Accordingly, the experiments that were conducted lead to recommending the use of sorption tubes to sample air being analyzed for SO_2, as replacements for the liquid absorption instruments in use at the present time. The advantages of sorption tubes include compactness, strength,

Table 2.

PASSAGE OF SO_2 THROUGH A TUBE (%) DURING TRAPPING BY A SORPTION TUBE AT -40°C AND USING AN ASPIRATION RATE OF 4 LITERS/MINUTE

Sequence no.	Composition of impregnating solutions	
	3% K_2CO_3, 15% ethylene glycol, 82% H_2O	3% K_2CO_3, 15% glycerine, 82% H_2O
1	1.2	2.4
2	1.0	2.1
3	0.9	3.3
4	1.3	1.9
5	1.3	3.6
Mean	1.1	2.7

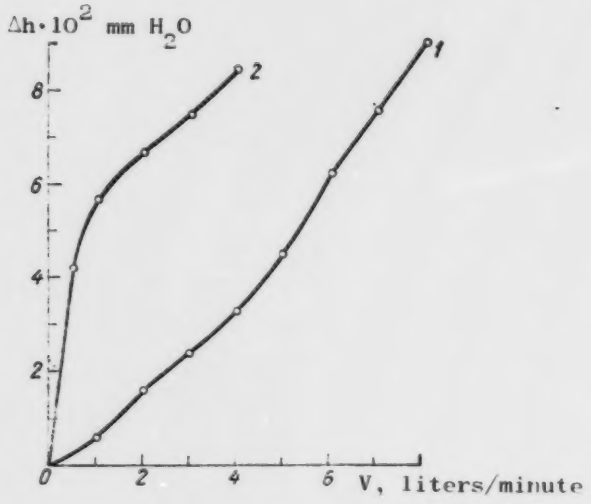

Figure 9. Resistance of absorption instrument as a function of flow of air being analyzed. 1 - sorption tube; 2 - standard absorption instrument with porous tile.

simplicity of manufacture and low cost, use of the mails for shipment, the possibility of pulling large volumes of air through the tubes (and as a result, making it possible to determine very low SO_2 concentrations), the possibility of sampling at temperatures below zero, and low air flow resistance.

The result of the research was the development of the following procedure for determining sulfur dioxide in a sample in a sorption tube.

The tube packing is impregnated with a 3% solution of K_2CO_3 in a 15% solution of glycerine, or ethylene glycol, in water. This is done by placing the tube in a beaker with the alkaline solution. A small quantity of the solution is drawn into the tube with a rubber bulb (so that the entire layer of glass powder is wetted). The excess solution is then blown out.

The impregnated tubes are kept in the vertical position for several hours (to allow the excess liquid to drain away), after which they are placed in test tubes with ground glass stoppers. A tube prepared in this manner is then used to sample the air to make the SO_2 determination.

If a one-time concentration of sulfur dioxide is to be made, the air to be analyzed is pulled through the tube at the rate of 2-6 liters/min for 20 minutes. An aerosol filter made of FPP-15 cloth is installed ahead of the tube to catch the aerosol of the sulfates. It is more advantageous to use a tube that has been impregnated with the ethylene glycol base in this case because it is more efficient.

Determination of the mean daily concentration involves pulling the air through at the rate of 1 liter/min for 24 hours. Here tubes that have been impregnated with the glycerine base should be used. The tube with the sample is placed in a test tube with a ground glass stopper and transported to the laboratory.

Once in the laboratory, the sorption tube is placed in a test tube containing 6 ml of a 0.3% solution of hydrogen peroxide. The solution is pumped through the sorption tube several times with a rubber bulb in order to oxidize the SO_2 and cause transfer into the solution in the form of the SO_4 ion to take place. The SO_4 ion concentration is found by the turbidometric method in terms of the intensity of the turbidity occurring upon the addition of barium chloride.

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